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(54) Liquid crystalline polyesters.

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ANGEWANDTE CHEMIE, vol. 23, September 1984, pages 690-703, Verlag Chemie GmbH,Weinheim, DE; D.J. WILLIAMS: "Organic polymeric and non-polymeric materialswith large optical nonlinearities"

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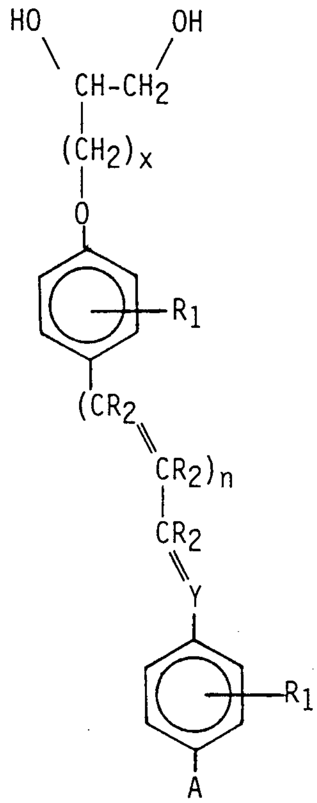
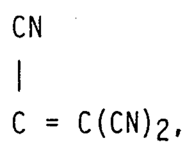
Description

The invention relates to liquid crystalline side-chain polyesters obtainable by polycondensing a diacid chloride with a diol of the formula



wherein

- R_1 = halogen, R_2, OR_2, COR_2, $COOR_2$, CN or CF_3;
- R_2 = H or an alkyl group having 1-3 carbon atoms;
- Y = CR_2, C-CN, or N;
- A = CN, NO_2, CH = $C(CN)_2$,



  or CF_3;
- n = 0-4.
- x = 0-6

Of course, the groups R_1 at the two benzene rings are not necessarily identical. This also applies to the groups R_2 at the double bonds.

Such diols display a molecular hyperpolarizability β of the order of 10^{-38} m^4/V. The phenomenon of molecular hyperpolarizability and the related non-linear optical (NLO) effects (Pockel's effect and second harmonic generation) are described in ACS Symposium Series 233, American Chemical Society, Washington D.C. 1983, and in Angew. Chem. 96 637-51(1984).

Generally, hyperpolarizable molecules have a delocalized π electron system to which both an electron donor group and an electron acceptor group are coupled directly (DπA system).

Polymers having hyperpolarizable side groups may be subjected to polar orientation in an electric field. As a result, the material also becomes macroscopically hyperpolarizable.
Such a material may be used in an optical switch, in which case an electric circuit is provided on a hyperpolarizable polymer. Such a use is described by J.I. Thackera et al., Appl. Phys. Lett. 52 1031-33-(1988).

So, the essence of the polyesters according to the invention is that they are prepared from diols having a DπA system. The group at the benzene ring (R_1) is not of vital importance here. Only if there should be a fluorine substituent at the ring to which the acceptor A is also coupled may, on the strength of European Patent Specification No. 0241 338, a real effect be expected on the macroscopic hyperpolarizability following the incorporation of the diol in a polymer. When selecting substituents at the double bond it should be kept in mind that the DπA system must not be forced out of planarity. If it is sterically forced out of planarity slightly by, for instance, a t-butyl group, then the hyperpolarizability may be influenced negatively.

Further, the polyester according to the invention are particularly suitable as a medium for optical data storage. In general, the use of liquid crystalline side-chain polymers for optical data storage is known from DE 3603267, which disclosure is incorporated herein by reference. In this respect the values of Tg (glass transition temperature) and Tc (clearing temperature) are of importance.
Tc is a concept known to the artisan and is used to characterize the thermodynamic stability of a liquid crystalline phase. It marks the transition from the anisotropic to the isotropic liquid phase.

Polyesters containing DπA groups of the aforementioned type are known from two papers by A.C. Griffin (SPIE Vol. 682, p. 65 (1986) Mol. Cryst. Liq. Cryst., vol. 155, 1988, pp. 129-139, published after the priority date). Such polyesters are prepared by polycondensation of an aliphatic diol with a diester to which a DπA system is attached.

It is advantageous that the polyesters according to the invention be based on NLO-active diols, as they need not be activated prior to polycondensation. Such activation is required for ester groups, which, for the DπA diesters described in the above-mentioned publication, means an additional reaction in the presence of the NLO-active group.

Thus, the diols according to the invention may be converted into a polyester by refluxing with a diacid chloride in, for instance, tetrahydrofuran (THF) for a period of about 1 hour. Polycondensation of the known diesters, on the other hand, requires the use of both a very low pressure and an elevated temperature (170 °C).

The above makes the use of diesters with elongated π systems (which exhibit the advantage of having a higher hyperpolarizability density) less atractive. If there are more double bonds, possible rearrangements under the required reaction conditions will cause the NLO activity to decrease.

For synthetic accessibility preference is given to those polyesters that are prepared from a diol of the aforesaid formula, wherein the spacer length $x = 1$.

In view of their small spacer length it may be considered surprising that these polyesters comprising mesogenically-substituted glycerol moieties are liquid crystalline and exhibit excellent Tg and Tc values. Also in view of the relatively high Tg and Tc values obtained, the polyesters according to the invention preferably are prepared from aliphatic diacids or derivatives and more preferably from glutaryl or adipoyl chloride.

Of course the polyesters according to the invention may be prepared from mixtures of diacid chloride. In preparing liquid crystalline polyesters it is allowed that these mixtures partly consist of aromatic dicarboxylic acids (or derivatives thereof). This may serve to raise the Tg of the polyester, but care should be taken that the polyester obtained still is liquid crystalline and has a Tc > Tg. Also, these mixtures may in part contain polyfunctional acid derivates so as to give a certain degree of branching, with the polymer still remaining processable. Alternatively, it is possible in polycondensation to make use of mixtures of diols, optionally mixed with non-NLO-active diols or polyols. Preferably, the percentage of NLO-active diols which is built into the polester is high enough to guarantee a hyperpolarizability density of at least 10^{-11} m^4/V.
By hyperpolarizability density is meant according to the invention the product of the number of hyperpolarizable groups per unit of volume and the molecular hyperpolarizability β_o of these groups. The β_o value indicates the molecular hyperpolarizability extrapolated to a frequency of zero. This is described by Katz et al in J.Am. Chem. Soc. 109 6561(1987).

The invention will be further described in but not limited by the following examples.

Example 1

Preparation of 4-(2,3-dihydroxypropyloxy)-4' -nitrostilbene

a. 4-hydroxy-4' -nitrostilbene

A mixture of 181 g of 4-nitrophenyl acetic acid, 122 g of 4-hydroxybenzaldehyde, 0,8 l of mesitylene and 0,2 l of piperidine was stirred for 90 minutes at 120 °C under an atmosphere of nitrogen. After cooling to 60 °C the reaction mixture was poured into a mixture of 1 l of 2N HCl and 1 l of petroleum ether (boiling point 80 °-110 °C). Following filtration and washing with 2 l of water the crude product was dried and then crystallized from 2 l of ethanol (100%). Obtained were 190 g of 4-hydroxy-4' -nitrostilbene having a melting point of 209 °C.

b. 4-((2,2-dimethyl-1,3-dioxa-4-cyclopentyl)methyl)-4' -nitrostilbene

A mixture of 120,5 g of 4-hydroxy-4' -nitrostilbene, 69 g of anhydrous potassium carbonate, 143 g of 2,2-dimethyl-4-(4-methyl phenyl sulphonyloxymethyl)-1,3-dioxolane, prepared in accordance with the specification of K. Freudenberg and H. Hess in Liebigs Annalen der Chemie Vol. 448 (1926), p. 121, and 1 l of dimethyl formamide (DMF) was boiled for 30 minutes with refluxing. After cooling the reaction mixture was poured, with vigorous stirring, into 5 l of water. The precipitated crystals were filtered off and after-washed with 5 l of water. The crude product after drying was crystallized from 4 l of acetone. Obtained were 135 g of 4-((2,2-dimethyl)-1,3-dioxa-4-cyclopentyl)methyl)-4'-nitrostilbene in the form of yellow acicular crystals having a melting point of 146 °-147 °C.

c. 4-(2,3-dihydroxypropyloxy)-4'-nitrostilbene

A solution of 135 g of 4-((2,2-dimethyl-1,3-dioxa-4-cyclopentyl)methyl)-4' -nitrostilbene, 15 g of para-toluene sulphonic acid monohydrate in 1 l of tetrahydrofuran (THF) and 100 ml of water was boiled with refluxing for 5 hours. After cooling the reaction mixture was neutralized with 10 ml of triethylamine. The resulting clear solution was concentrated by evaporation to a volume of about 0,5 l and subsequently poured, with vigorous stirring, into 5 l of water. The resulting precipitate was filtered off and after-washed with 5 l of water. The crude product after drying was crystallized from a mixture of 2 l of acetone and 0,5 l of n-hexane. Obtained were 105 g of 4-(2,3-dihydroxypropyloxy)-4'-nitrostilbene having a melting point of 147 °C and a clearing temperature of 152 °C.

Example 2

Preparation of 4-(2,3-dihydroxypropyloxy)-4'-cyanostilbene

a. 4-(2,2-dimethyl-1,3-dioxa-4-cyclopentyl)methyloxy)benzaldehyde

A mixture of 122 g of 4-hydroxybenzaldehyde, 69 g of anhydrous potassium carbonate, 286 g of 2,2-dimethyl-4-(4-methyl phenyl sulphonyloxy methyl)-1,3-dioxolane, prepared in accordance with the specification of K. Freudenberg en H. Hess in Liebigs Annalen der Chemie, Vol. 448(1926), p. 121, and 0,5 l of dimethyl formamide was boiled with refluxing for 60 minutes. After cooling, the reaction mixture was poured, with vigorous stirring, into 2,5 l of water. The precipitated crystals were filtered off and thoroughly washed with water. The crude product was recrystallized from isopropanol. Obtained were 150 g of 4-((2,2-dimethyl-1,3dioxa-4-cyclopentyl)methyloxy)benzaldehyde with a melting point of 44 °-47 °C.

b. 4-(2,3-dihydroxypropyloxy)-4' -cyanostilbene

To a solution of 47,2 g of 4-((2,2-dimethyl-1,3dioxa-4-cyclopentyl)-methyloxy) benzaldehyde in 400 ml of dimethyl formamide were added 50,6 g of diethyl 4-cyanophenyl phosphonate, prepared in accordance with the specification of A. Franke et al. in Synthesis (1979), p. 712-714, and (in small portions) 10 g of sodium hydride, 60%-dispersion in mineral oil. The reaction mixture was stirred for 1 hour at room temperature and subsequently neutralized with diluted acetic acid. The resulting mixture was concentrated to a small volume, taken up in 1 l of dichloromethane, and washed with a 10%-aqueous solution of sodium bicarbonate and water. The organic layer was separated, dried on magnesium sulfate, and evaporated. The crude product, consisting of 65 g of almost pure 4-((2,2-dimethyl-1,3-dioxa-4-cyclopentyl)methyloxy)-4'-cyanostilbene was added to a mixture of 400 ml of tetrahydrofuran, 40 ml of water, and 10 ml of concentrated hydrochloric acid. The resulting mixture was boiled with refluxing for 2 hours. After cooling it was neutralized with triethyl amine, concentrated to a small volume, and poured, with vigorous stirring, into 2 l of water. The precipitated product was filtered off, dried in vacuo, and crystallized from a mixture of 100 ml of dimethyl formamide and 100 ml of ethanol. The yield was 42 g, of pure 4-(2,3-dihydroxypropyloxy)-4'-cyanostilbene with a melting point of 172 °-173 °C.

Example 3

Preparation of 4-(2,3-dihydroxypropyloxy)-2'-fluoro-4'-nitrostilbene

2-Fluoro-4-nitrotoluene (commercially available) was converted with the use of N-bromosuccimimide into the intermediate 2-fluoro-4-nitrobenzyl bromide, and subsequently into diethyl 2-fluoro-4-nitrobenzyl-phosphonate, in accordance with the specification of D.H. Wadsworth et al. in the Journal of Organic Chemistry, Vol. 30 (1965) p. 680-685. The title compound was prepared by the same procedure as described in Example 2. Making use of 23,6 g of 4-((2,2-dimethyl-1,3-dioxa-4-cyclopentyl)methyloxy)-benzaldehyde and 29,1 g of diethyl 2-fluoro-4-nitrobenzyl phosphonate there were obtained in all 21 g of 4-(2,3-dihydroxypropyloxy)-2'-fluoro-4'-nitrostilbene with a melting point of 110 °C and a clearing temperature of 129 °C.

Example 4

General preparation of NLO-polyesters

To a mixture of 10 mmoles of monomeric diol (see Examples 1, 2 and 3), 3 ml of tetrahydrofuran, and 10 mmoles of freshly distilled diacid chloride (see Table 1) were added 3 ml of pyridine. The reaction mixture was boiled with refluxing for 1 hour and, after cooling, poured into 500 ml of water. The precipitated product was filtered off, washed thoroughly with methanol, and dried in vacuo at 50 °C. The yields were almost quantitative.

Table 1: Data on NLO polyesters

monomers		M_W a)	Tg	Tc	Dhyp in b)
diol from Example No.	diacid chloride		(in °C)		10^{-11} m V
1	glutaryl	4300	59	105	2.8
1	adipoyl	4700	56	88	2.7
1	suberyl	8000	40	69	2.5
1	sebacyl	12000	42	62	2.4
2	adipoyl	4400	52	103	0.3
3	adipoyl	3400	41	63	2.7

a) The M_W was determined by gel permeation chromatography, the calibration curve being plotted using a series of polystyrene standard samples of a known molecular weight.

b) Hyperpolarizability density.

$$D_{hyp} = \frac{\varrho N_A}{M} \cdot \beta_o$$

ϱ: density, for which a value of 1.2 10^6 g m^{-3} is taken

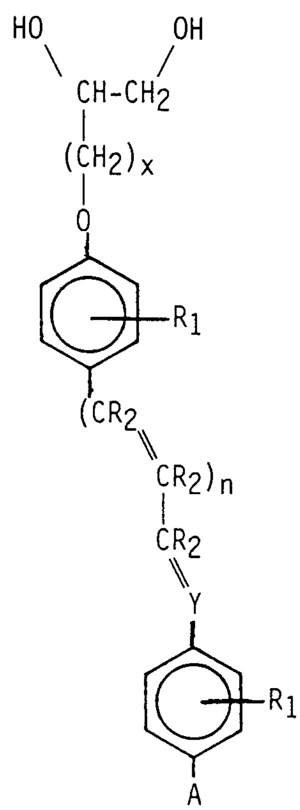
N_A: Avogadro number (6 10^{23} $mol.^{-1}$)

M: Molecular weight of the recurring unit in g $mol.^{-1}$

β_o: molecular hyperpolarizability extrapolated to a frequency of zero in accordance with the publication by Katz et al. referred to above.

Claims

1. A polyester obtainable by polycondensing a diacid chloride with a diol of the formula:



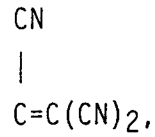
wherein

R_1 = halogen, R_2, OR_2, COR_2, $COOR_2$, CN or CF_3;

R_2 = H or an alkyl group having 1-3 carbon atoms;

Y = CR_2, C-CN, or N;

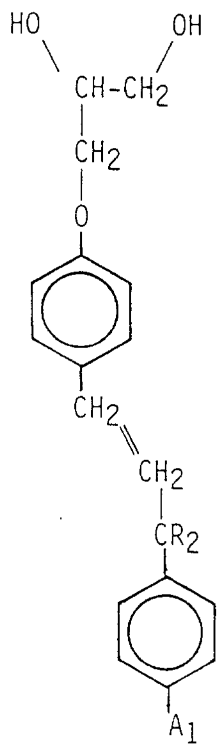
A = CN, NO_2, CH = $C(CN)_2$,



or CF_3;
n = 0-4.
x = 0-6

2. A polyester according to claim 1, characterized in that the dicarboxylic acid or derivative thereof is substantially an aliphatic diacid.

3. A polyester according to claim 1, characterized in that the dicarboxylic acid derivative is adipoyl or glutaryl chloride and the diol is of the formula



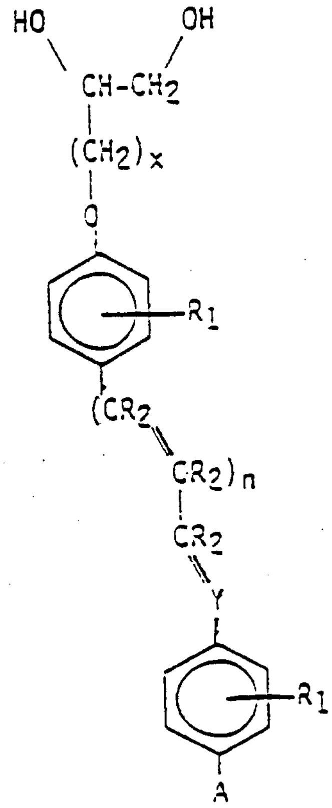
wherein
A_1 = CN or NO_2

4. An optical waveguide, characterized in that it is of a polyester according to claim 1, 2 or 3.

5. A medium for optical data storage, characterized in that it is of a polyester according to claim 1, 2 or 3.

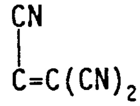
Patentansprüche

1. Polyester, erhältlich durch Polykondensieren eines Disäurechlorids mit einem Diol der Formel



worin

R_1	= Halogen, R_2, OR_2, COR_2, $COOR_2$, CN oder CF_3;
R_2	= H oder eine Alkylgruppe mit 1-3 Kohlenstoffatomen;
Y	= CR_2, C-CN oder N;
A	= CN, NO_2, $CH=C(CN)_2$,

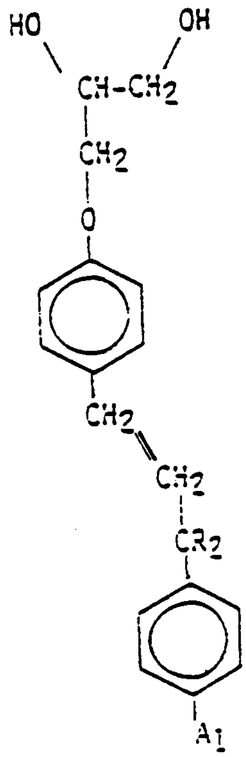


oder CF_3

n	= 0-4
x	= 0-6.

2. Polyester nach Anspruch 1, dadurch gekennzeichnet, dass die Dicarbonsäure oder deren Derivat im wesentlichen eine aliphatische Disäure ist.

3. Polyester nach Anspruch 1, dadurch gekennzeichnet, dass das Dicarbonsäurederivat Adipinsäure- oder Glutarsäurechlorid ist und das Diol der folgenden Formel entspricht:



worin

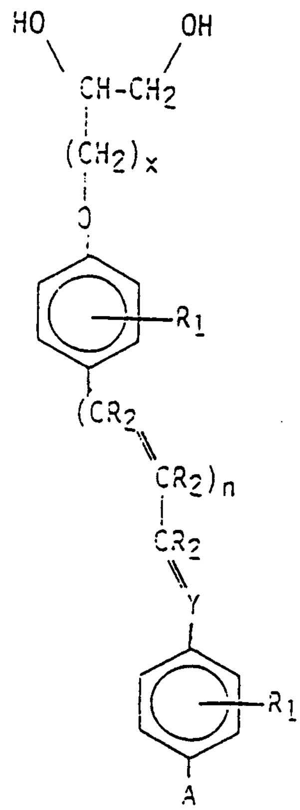
A_1 = CN oder NO_2.

4. Optischer Wellenleiter, dadurch gekennzeichnet, dass er aus einem Polyester gemäss den Ansprüchen 1, 2 oder 3 besteht.

5. Medium für optische Datenspeicherung, dadurch gekennzeichnet, dass es aus einem Polyester nach den Ansprüchen 1, 2 oder 3 besteht.

Revendications

1. Un polyester susceptible d'être obtenu par polycondensation d'un chlorure de diacide avec un diol représenté par la formule:



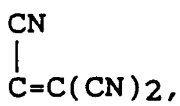
dans laquelle

R_1 représente un atome d'halogène, R_2, OR_2, COR_2, $COOR_2$, CN ou CF_3;

R_2 représente un atome d'hydrogène ou un radical alkyle comportant de 1 à 3 atomes de carbone;

Y représente CR_2, C-CN, ou N;

A représente CN, NO_2, CH = C(CN)2,



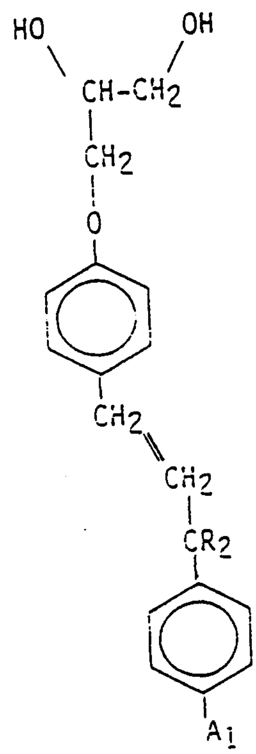
ou CF_3;

n est un nombre de 0 à 4.

x est un nombre de 0 à 6.

2. Un polyester selon la revendication 1, caractérisé en ce que l'acide dicarboxylique ou le dérivé de ce dernier correspond sensiblement à un diacide aliphatique.

3. Un polyester selon la revendication 1, caractérisé en ce que le dérivé d'acide dicarboxylique est un chlorure d'adipoyle ou de glutaryle et le diol est représenté par la formule



dans laquelle A_1 représente CN ou NO_2.

4. Un guide d'onde optique caractérisé en ce qu'il est constitué d'un polyester selon la revendication 1, 2 ou 3.

5. Un milieu pour le stockage des données optiques caractérisé en ce qu'il est constitué d'un polyester selon la revendication 1, 2 ou 3.